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A green and sustainable approach for esterification of glycerol using 12-tungstophosphoric acid anchored to different supports: Kinetics and effect of support

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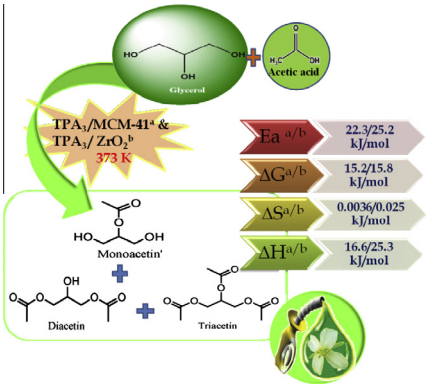
HIGHLIGHTS

- Synthesis of 12-tungstophosphoric acid anchored to MCM-41 and zirconia.
- Thermal and textural characterization.
- Glycerol esterification to yield useful glycerol ester products.
- Kinetic and thermodynamic parameters optimized.
- Potential of being used as recyclable catalysts after simple regeneration.

GRAPHICAL ABSTRACT



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ABSTRACT

Environmentally benign solid acid catalysts consisting of 12-tungstophosphoric anchored to MCM-41 and zirconia were synthesized and characterized. The efficacy for the esterification of glycerol, a value added byproduct from biodiesel production was investigated. Conditions for maximum conversion was optimized by varying different reaction parameters, such as, glycerol/acetic acid mole ratio, amount of the catalyst, reaction time and reaction temperature. The kinetic study was carried out, and it was found that esterification of glycerol follows first order kinetics and the rates are not mass transfer limited. Also activation energy and ΔG was determined. The difference in % conversion as well as selectivity was correlated with the nature of supports, value of activation energy as well as ΔG. The catalysts showed potential of being used as recyclable material after simple regeneration without significant loss in conversion.

1. Introduction

Due to tremendous increase in the research and demand for biodiesel production, surplus of glycerol as a byproduct has accumulated in the biodiesel market. This leads to a glut of glycerol in the market, as well as increase in the price of biofuel. Glycerol, as such is a raw material for the production of food additives, cosmetic ingredients and surfactants. But these markets are insufficient to consume all the glycerol generated from biodiesel industry. This situation has prompted excessive search for new, easy and sustainable conversions of glycerol as well as its uses. To fill the gap between sustainability and utilization of excess left over glycerol, the esterification of glycerol is one of the alternatives.

Glycerol esters have a wide variety of applications as solvents, as emulsifying and stabilizing compounds, as raw materials in food, and the cosmetic and pharmaceutical industries [1]. Monoacetylglycerol (MAG) is used in the manufacture of explosives, in

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Nomenclature

List of Symbols

°C	degree celsius
Ea	activation energy
θ	theta (scanning angle)
k	rate constant
ΔG	Gibbs free energy
ΔH	enthalpy
ΔS	entropy
R	gas constant
A	pre-exponential factor
R^2	correlation coefficient
Keq	equilibrium constant

tanning, and as solvents for dyes. Diacetylglycerol (DAG) is used as a plasticizer and softening agent and solvent [2]. Triacetylglycerol (TAG) is used as a solvent, antimicrobial and emulsifying agent in cigarette filters, pharmaceuticals. DAG and TAG also improve the properties of biodiesel (e.g., cold flow and viscosity properties) or gasoline (e.g., antiknocking properties) [3].

From the view point of 'Green Chemistry' or 'Sustainable Technology', number of heterogeneous catalysts such as Zeolite , Amberlyst-15 , niobic acid [4], Starbon acid, Sulfated activated carbon [5], ion exchange resins [6], functionalized mesoporous silica-type SBA-15, mesoporous silica MCM-41 sulphonated and functionalized with different alkyl chains (methyl, ethyl, propyl and phenyl) [7], Zirconia based solid acid catalysts [8], Hydroxylated magnesium fluorides [9] have been reported for the esterification of glycerol. A new avenue for continuous esterification of glycerol with acetic acid in supercritical carbon dioxide ($scCO_2$) was also investigated [10]. Some of the above reactions comprising of sulfated activated carbon, ion exchange resins, Amberlyst etc. are marked by the limitation of high reaction pressure, temperature (120 °C) and activation of the catalysts, which poses a question on sustainability.

A literature survey shows that Dodecatungstophosphoric acid immobilized on silica matrix was used as catalyst [11], also activated carbon was used as support by the same group [12]. The catalytic activity of glycerol esterification was studied over Dodecamolybdophosphoric acid encaged in USY zeolite [13]. Addition to these catalysts, niobic acid supported heteropolytungstate [14], heteropolytungstate supported on Cs-containing zirconia [15], hybrid SBA-15 functionalized with molybdophosphoric acid [16], and zirconia supported heteropolyacids-HPAs (HSiW, HPW and HPMo) [17] have also been used. Although the conversions and selectivity's towards the esters are good, new methods are needed to be explored wherein the reaction can proceed even at relatively lower molar ratios, catalyst amounts and temperatures. Thus it is still a challenge to design a green and sustainable process for the same.

In this direction an attempt was made to carry out esterification of glycerol using environmentally benign catalysts, under green conditions. We are working on supported and anchored HPA since last one decade and we have reported number of organic transformations using different supported/anchored HPAs [18,19]. As an extension of our work, here we are exploring the use of 12-tungstophosphoric acid (TPA) anchored to Zirconia and MCM-41 for esterification of glycerol, green and sustainable approach.

The effect of various reaction parameters such as glycerol/acid molar ratio, amount of catalyst, reaction time and temperature was studied to optimize the conditions for maximum conversion of glycerol and selectivity towards its esters. Further we are also reporting kinetic study as well as Koros Nowak test. Koros Nowak test was carried out to identify heat or mass transfer limitations in measurements of catalytic rates. From kinetic study it was found that the esterification reaction of glycerol with acetic acid follows a first order dependency on the concentration of glycerol and the catalyst. The influence of temperature on rate constant was studied and the activation energy (*Ea*) was also calculated. The difference in conversion and selectivity over both the catalysts were correlated with the nature of support and value of Gibbs free energy (ΔG) for esterification reaction. Also catalysts were recycled, regenerated and reused up to four cycles.

2. Experimental

2.1. Preparation of the supports and catalyst

2.1.1. Materials

All chemicals used were of A.R. grade. 12-tungstophosphoric acid (TPA), $ZrOCl_2{\cdot}8H_2O$ (Zirconium oxychloride), liquor ammonia, CTAB (Cetyltrimethyl ammonium bromide), TEOS (tetraethyl orthosilicate), glycerol, and acetic acid were used as received from Merck.

2.1.2. Synthesis of the supports

MCM-41 was synthesized by following procedure reported by us [20]. Surfactant (CTAB) was added to the very dilute solution of NaOH with stirring at 60 °C. When the solution became homogeneous, TEOS was added drop wise, and the obtained gel was aged for 2 h. The resulting product was filtered, washed with distilled water, and then dried at room temperature. The obtained material was calcined at 550 °C in air for 5 h and designated as MCM-41.

Hydrous zirconia was prepared by following method reported by us [21]. Aqueous ammonia solution was added to aqueous solution of $ZrOCl_2{\cdot}8H_2O$ up to pH 8.5. The precipitates were aged at 100 °C over a water bath for 1 h, filtered, washed with conductivity water until chloride free water was obtained and dried at 100 °C for 10 h. The obtained material is designated as ZrO_2.

2.1.3. Synthesis of the catalysts (TPA Anchored to MCM-41 and ZrO_2)

Two series of catalysts containing 10–40% of TPA anchored to MCM-41 and Zirconia were synthesized by incipient impregnation method. One g of MCM-41 was impregnated with an aqueous solution of TPA (0.1/10−0.4/40 g/mL of double distilled water) and dried at 100 °C for 10 h. The obtained materials were designated as TPA_1/MCM-41, TPA_2/MCM-41, TPA_3/MCM-41, and TPA_4/MCM-41, respectively. A series of catalysts containing 10–40% of TPA anchored to ZrO_2 was synthesized following the same method. The obtained materials were designated as TPA_1/ZrO_2, TPA_2/ZrO_2, TPA_3/ZrO_2, and TPA_4/ZrO_2, respectively.

2.2. Characterization

A detailed study on the characterizations of all the synthesized catalysts can be found in our earlier publications [20,21]. However in the present article EDS, TGA, BET, XRD, NH_3-TPD acidity measurements are given for reader's convenience.

Elemental analysis was carried out using JSM 5910 LV combined with an INCA instrument for EDS. Thermo gravimetric analysis (TGA) of the samples was carried out on a Mettler Toledo Star